



U.S. Department of Energy
Energy Efficiency and Renewable Energy

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Verification of Syngas Quality

**DOE OBP Thermochemical Platform Review
Meeting
June 7-8, 2005**

**James White, PNNL
Steve Deutch, NREL**



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- **Project Background**
- **Technical Feasibility and Risks**
- **Competitive Advantage**
- **Project Overview**
- **History and Accomplishments**
- **Plan/Schedule**
- **Critical Issues and Show-stoppers**
- **Plans and Resources for Next Stage**
- **Summary**

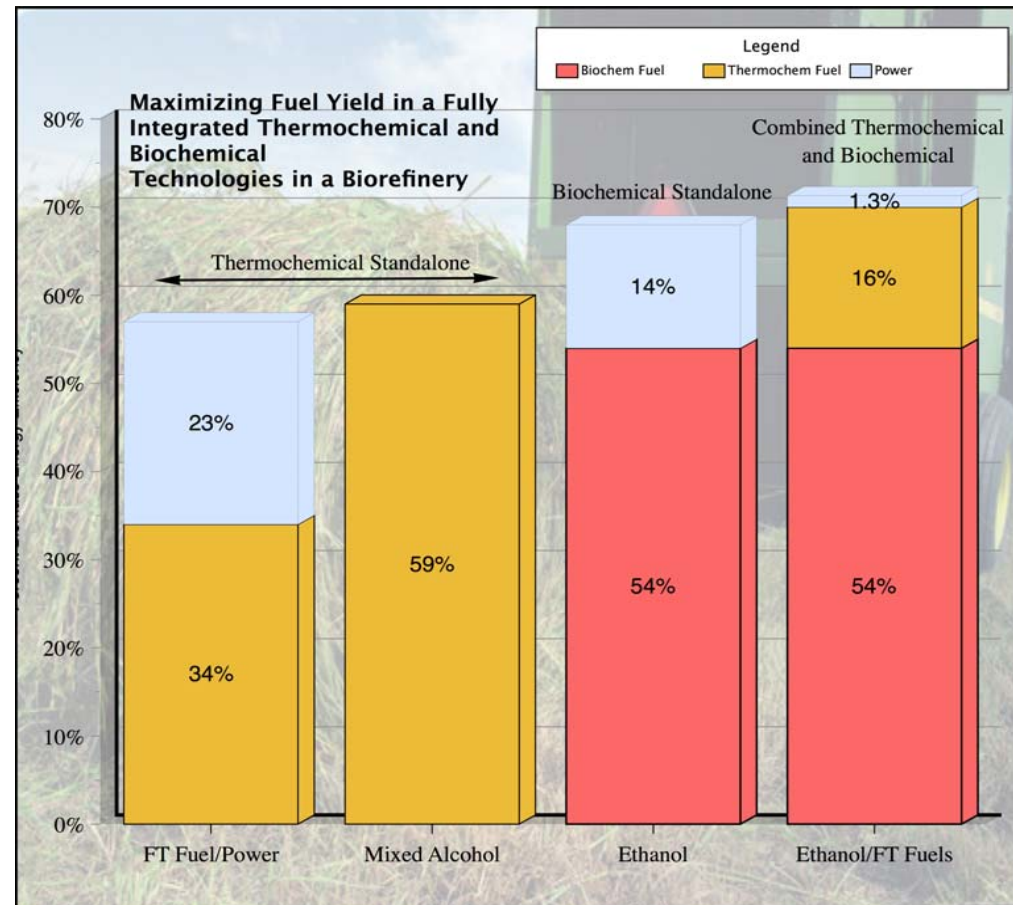


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Analysis in 2004/2005 identified mixed alcohols as a biorefinery opportunity

Mixed alcohols provide:

- High conversion efficiency to fuels
- Synergistic mix of fuel and chemicals
 - Ethanol for fuel
 - Propanol
 - Butanol
 - Other higher alcohols
- Low cost of recovery and separation





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- Previous work on mixed alcohols was not directed toward biomass systems
 - Didn't address biomass resources or biomass syngas (different slate of impurities)
 - Didn't attempt to maximize product values in the biorefinery
- NREL and PNNL are working to verify the utilization of syngas for mixed alcohol production
 - Effort re-oriented for 2005
 - Lab-scale work on mixed alcohol catalysts
 - Initial focus on commercial or near-commercial samples
 - Effort began in late May 2005



Pathways and Milestones – C-level and Project Milestones

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Aq Residues

Perennial Grasses

Woody Crops

Pulp and Paper

Forest Products

Validate Cost-effective Gas Cleanup Performance

Validate integrated gasification and gas cleanup at pilot scale

Project Milestones	Type	Performance Expectations	Due Date
Mixed OH Catalyst Evaluation	E	In collaboration with industry, select initial catalysts for evaluation	8/30/05
Mixed OH Reactor shakedown	E	Complete installation and shakedown of high pressure fuels synthesis reactor to evaluate syngas quality	9/30/05



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Current Technical challenges

- **Productivity of mixed alcohol catalysts**
 - Improvements in space time Yield (STY) would be helpful
 - Catalyst companies are not currently active in the area
- **Selectivity of mixed alcohol catalysts**
 - Need the right mix of fuels and chemicals to ensure economic return in the integrated biorefinery
 - Adjustable product selectivity would be useful
- **Verification with actual biomass syngas**
 - Experimental data needed to support analysis activities



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- **Results of successful fuel/chemical alcohol production**
 - Improved conversion of biomass to ethanol, a fully accepted gasoline replacement
 - Production of butanol and propanol as higher valued chemicals to provide additional profits
 - Project will provide needed technical data to verify feasibility of this approach
- **Competition**
 - Break-through technologies for biological conversion of lignin
 - Break-through advances in syngas fermentation



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Project Goal:

- **Verify the feasibility of producing mixed alcohol products from biomass derived syngas in an integrated biorefinery**
 - Identify and down-select “existing” catalysts most suitable for the biorefinery
 - Test selected catalysts with slipstream of biomass syngas
 - Conduct combinatorial experiments to improve catalyst productivity and determine appropriate product range
- This effort results from refocus of thermal conversion program



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FY05 Plan:

- **Catalyst Selection (NREL & PNNL)**
 - Identify and down-select the most promising “existing” mixed alcohol catalysts
 - Obtain samples from catalyst manufacturers where/if possible
- **Catalyst validation and improvement (PNNL)**
 - Produce lab quantities of catalysts as needed
 - Obtain catalyst performance data using bottled gas to identify the most promising catalysts for biomass
 - Use initial results to begin planning catalyst improvement studies
- **Catalyst validation with biomass syngas (NREL)**
 - Complete assembly of synthesis fixed bed reactor
 - Conduct initial shake-down test of the synthesis reactor with biomass syngas using a known catalyst (methanol)



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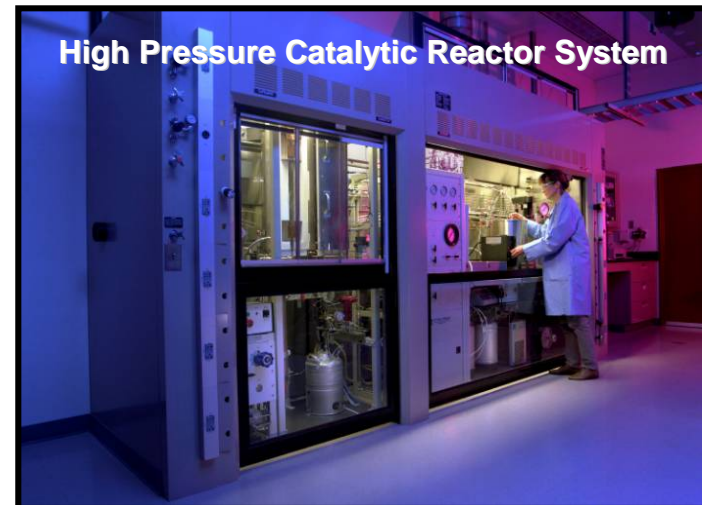
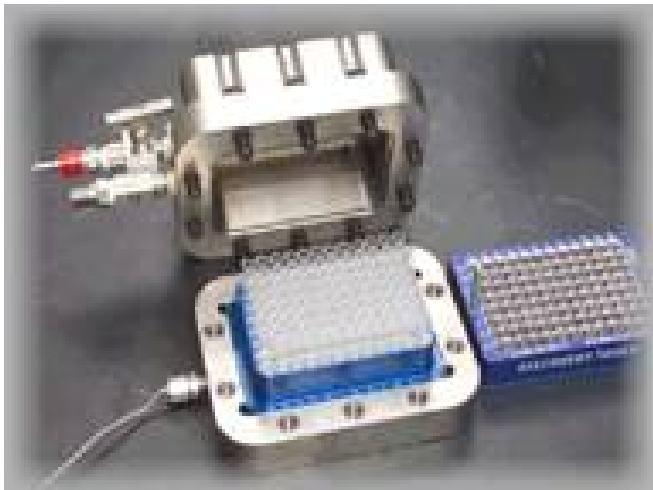
FY06 Plan (NREL & PNNL):

- Conduct combinatorial studies to improve catalyst productivity (STY)
- Prepare quantities of selected catalysts for use at NREL
- Test mixed alcohol production using initial catalysts and syngas from biomass gasifier
- Begin gasifier/synthesis tests using biomass syngas
- Use results to assist with more detailed techno-economic analysis



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- **PNNL reactor systems**
 - Multiple batch autoclaves (100cc to 1000cc to 3000psig/300°C)
 - Multiple continuous fixed bed flow reactors (0.5 cc to 1000 cc, to 3000psig / 400°C)
 - Combinatorial (batch, 2000 psig/200°C)





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Catalyst characterization tools are available at PNNL

- **Surface science:**
XPS, AUGER, SIMMS, RAMAN, SEM/STEM, AFM
- **Other:**
XRD, MAS-NMR, Chemisorption-Mass Spec, STA-Mass Spec, Hg and N₂ Porosimetry



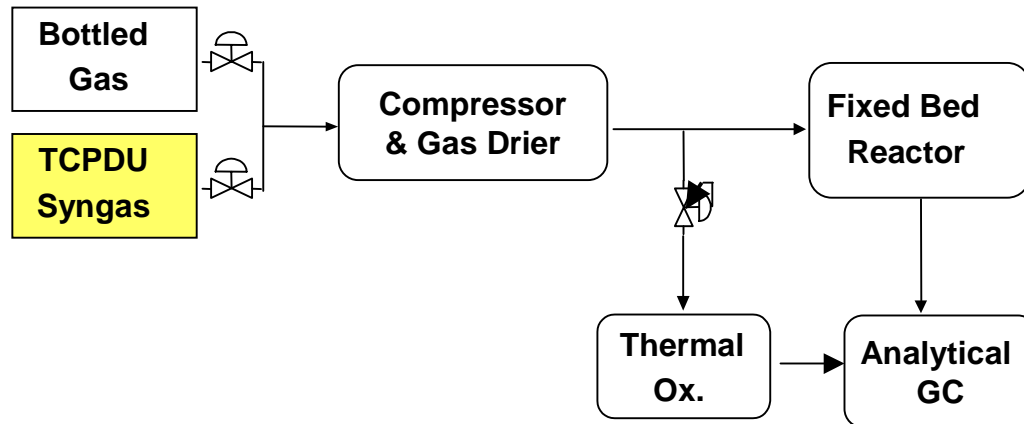
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Gasification and synthesis reactors are available at NREL

- Fixed-bed synthesis reactor is being installed
- Can use bottled syngas or biomass syngas from the NREL gasifier



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- Major components

H_2 , CO , CO_2 , CH_4 , C_2H_4

- Minor components

C_2H_6 , C_2H_2 , $C_3=$, $C_4=$

- Trace components

Aromatics, Phenolics, "Tars"

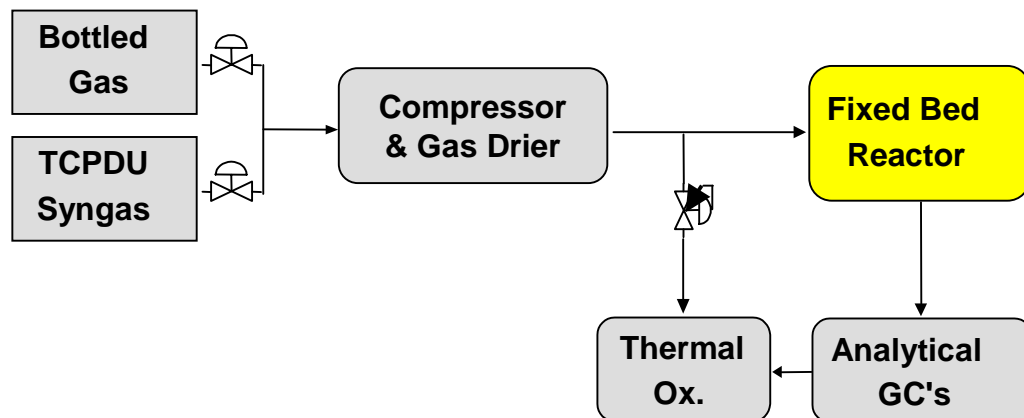
HCl , H_2S , HCN , NH_3





NREL Fuels & Chemicals Synthesis Fixed Bed Reactor

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- **260 bar MWP**
- **650°C reactor temperature**
- **19 x 300 mm tubular reactor**
- **Condensation system**
- **Heated GC transfer line**
- **Productivity ~10's grams/hr**





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High Pressure Fixed Bed Reactor System

- Enclosure installed – 5' x 5' x 7' room, 2-hr fire rating, fire stop louvers
- Major Equipment installed – Fixed bed reactor system, high pressure compressor, low pressure compressor, Agilent GC and MTI MicroGC
- System fabrication and safety/readiness verification completed 5/05
- Shakedown and system availability expected 6/05



Critical Issues and Show-stoppers

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- **Performance parameters:**
 - Syngas quality
 - Syngas quality must be met (acceptable sulfur/tar/heteroatom, CO₂ tolerance levels vary by catalyst)
 - Catalyst productivity – increase to 0.8-1.0 STY desirable
 - Ethanol and higher alcohols purity – maintain low sulfur levels if sulfided catalysts are used
- **Potential show stoppers:**
 - Unforeseen catalyst problems with biomass syngas



Plans and Resources for Next Stage

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- **Beyond 2006:**
 - Stage gate review to determine future effort
 - Work with industries related to the ethanol production
 - Work with the catalyst industry to ensure that catalysts are available



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- Synthesis of mixed alcohols that would be separated for fuel and chemical uses appears to have potential for the integrated biorefinery
- Verification studies will help quantify this potential
- Project funding:
FY05:
 - NREL \$ 200K
 - PNNL \$ 200K